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TITLE: INFRARED ABSORBING BLUE GLASS COMPOSITION

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INFRARED ABSORBING BLUE GLASS COMPOSITION

[0001] The invention relates to a blue soda-lime-silica glass composition that contains a colorant portion comprising iron oxide and cobalt oxide and further comprising manganese oxide to reduce amber color attributed to reaction of iron oxide with sulfate refining agents.

BACKGROUND OF THE INVENTION

[0002] It would be advantageous to improve infrared (IR) and ultraviolet (UV) absorption of soda-lime-silica glass products while maintaining a high visible transmission. For example, automotive vehicles require glass having high visible transmittance to assure optimum visibility for the operator. Infrared and ultraviolet light do not improve visibility, but generate heat within the passenger compartment and, particularly during summertime driving, increase the load on the air conditioning system to maintain comfort levels.

[0003] Iron oxide is commonly added to glass to produce a green color. In glass, iron oxide is found in two chemical forms. The oxidized compound is ferric oxide, Fe_2O_3, and is yellow. The reduced compound is ferrous oxide, FeO, and is blue. Advantageously, ferric oxide absorbs a portion of ultraviolet light passing through the glass product; and ferrous oxide absorbs a portion of infrared light passing through the glass product. Under typical furnace melting conditions, when the total iron oxide in the glass product is within the range of about 0.3 to 0.8 weight percent, the iron oxide equilibrium is such that the redox ratio of FeO to total iron oxide is about 0.23 to 0.26, which imparts a green color to the glass. As used herein, total iron oxide refers to weight of an equivalent amount of iron as ferrous

oxide, Fe_2O_3. Also, as used herein, compositional percentages are based upon weight, except as otherwise noted.

[0004] During melting, it is common practice to add a sulfate compound, typically sodium sulfate, and a carbonaceous material, typically anthracite coal, for refining purposes. In the presence of carbon, the sulfate compound dissociates to form sulfur oxide that facilitates the removal of bubbles from the molten glass, which would otherwise produce defects in the product.

[0005] It is also desirable to produce glass having a dark blue coloration for aesthetic purposes. It is known that increasing the proportion of ferrous oxide relative to ferric oxide shifts the glass color from green to blue. This is readily accomplished by increasing the addition of carbonaceous material to the glass melt, whereupon the additional carbon reacts with ferric oxide to form additional ferrous oxide. However, decreasing the ferrous oxide reduces infrared absorption by the glass. Moreover, attempts to compensate by increasing the total iron concentration to maintain a high infrared absorption reduces visible transmittance of the glass and is not desired. This is attributed, in part, to a reaction between iron and sulfur derived from the sulfate refining agent to produce iron sulfide, which imparts an amber coloration that dramatically decreases visible transmittance and also shifts the color of the glass so that the desired aesthetically blue coloration is not achieved. It is also known to produce blue glass by additions of cobalt oxide. However, when added to glass containing iron sulfide, the amber coloration shifts the dominant wavelength away from the desired blue range and reduces visible transmittance.

[0006] Therefore, a need exists for a glass having enhanced blue coloration as indicated by a high excitation purity that is not diminished by iron sulfide amber or

other non-blue coloration, and which further exhibits a high visible transmittance and high infrared absorption.

SUMMARY OF THE INVENTION

[0007] The present invention is a blue glass composition that comprises a soda-lime-silica base and a colorant portion consisting essentially of about 0.4 to 0.65 wt.% total iron oxide, reported as Fe_2O_3; about 0.1 to 0.3 weight percent manganese oxide reported as MnO_2 ; and cobalt oxide in an amount effective to produce a cobalt concentration of about 0.0002 to 0.0013 weight percent (about 2 to 13 ppm). The iron oxide includes significant concentrations of both ferric oxide and ferrous oxide, such that the ratio of FeO to total iron oxide is between about 0.43 and 0.58. As used herein, iron and manganese concentrations are reported based upon weights of equivalent amounts of Fe_2O_3 and MnO, respectively, whereas cobalt additions are reported based upon elemental weight.

[0008] Glass compositions according to this invention have the following spectral properties, measured at 4.0 mm thickness: about 68 to 76 percent Illuminant A transmittance (LTA); about 54 to 64 percent ultraviolet transmittance; about 12 to 22 percent infrared transmittance; about 38 to 47 percent total solar energy transmittance; a dominant wavelength between about 486 and 490 nanometers, preferably between 488 and 489 nanometers; and an excitation purity between about 7 and 11 percent.

[0009] Thus, glass composition in accordance to this invention exhibits an unexpected combination of high visible transmittance, high infrared absorption, and enhanced blue coloration. The enhanced blue coloration is demonstrated by the dominant wavelength in the blue spectrum and the relatively high excitation purity,

and is attributed to the combination of ferrous oxide and cobalt oxide. The increased ferrous proportion, indicated by the relatively high redox ratio, also results in high infrared absorption. It is unexpectedly found that, despite the relatively high ferrous content, as well as the cobalt oxide presence, the manganese oxide addition is effective to reduce iron sulfide formation and thus avoid amber coloration. Still further, the cobalt oxide levels, with presence of ferrous oxide, are effective to enhance blue coloration, while being suitably low to avoid reducing visible transmittance. Thus, blue glass in accordance with this invention is particularly well suited for automotive or architectural use to provide an aesthetically pleasing appearance and high visible transmittance, while absorbing infrared radiation to reduce solar heating and thus the load on air conditioning systems required to cool compartments having windows formed of the glass.

DETAILED DESCRIPTION OF THE INVENTION

[0010] In accordance with a preferred embodiment of this invention, flat soda-lime-silica glass having an enhanced blue coloration is provided to use as automotive or architectural glazing. The blue glass comprises a soda-lime-silica base to which colorant is added and is conveniently made by the float glass process. A preferred base is composed of between about 68 to 75 weight percent SiO_2, 0 to about 5 weight percent Al_2O_3, about 5 to 15 weight percent CaO, 0 to about 10 weight percent MgO, about 10 to 18 weight percent Na_2O and 0 to about 5 weight percent K_2O. The preferred base is further characterized by a total CaO and MgO between about 6 to 15 weight percent and a total Na_2O and K_2O between about 10 to 20 weight percent. Preferably SO_3 is between about 0.03 to 0.12 weight percent, more preferably between about 0.05 to 0.08 weight percent.

[0011] Blue glass in accordance with this invention also contains a colorant portion comprising iron oxide, manganese compound; and cobalt oxide.

[0012] Iron oxide is added in an amount effective to reduce ultraviolet and infrared transmittance. The total iron oxide, reported as Fe_2O_3, is preferably between about 0.4 to 0.65 weight percent. The iron oxide is conveniently added as ferric oxide and reacts with carbon or other reducing agents added to the melt during processing to form ferrous oxide. The proportion of ferrous oxide is characterized by the redox ratio, which the proportion by weight of FeO to total iron oxide, and is preferably between about 0.43 to 0.58.

[0013] It is found that the addition of manganese compound suppresses iron sulfide formation which would otherwise result from reaction between ferrous iron and sulfur derived from sulfate refining agents added to the glass melt during processing and produce undesirable amber coloration. Preferably, manganese is added in an amount between about 0.1 to 0.3 weight percent based on MnO_2. Manganese may be readily added in any suitable form, including MnO_2, Mn_3O_4, MnO, $MnCO_3$, $MnSO_4$, MnF_2, and $MnCl_2$.

[0014] The blue glass composition is preferably formed as a melt using a sulfate refining agent. Raising the redox ratio above the preferred range, particularly about 0.62, tends to result in formation of iron sulfide and the presence of the amber chromophore. In accordance with this invention, the blue glass composition contains cobalt oxide to enhance blue coloration without the undesired amber. Preferred cobalt content is between about 0.0002 and 0.0013 weight percent (2 and 13 ppm). More preferably, it is found that additions between about 0.0003 and 0.0010 weight percent (3 and 10 ppm) cobalt are effective to produce uniform and

consistent coloration despite variation in the iron oxide content within the preferred ranges, while avoiding effects of cobalt on other glass properties.

[0015] The blue glass composition is preferably formed by a batch mixing process wherein raw materials are admixed and melted and the melt is feed to a conventional float glass furnace. By way of a preferred example, blue glass is made by admixing the raw materials in Table I within the recited ranges.

TABLE I

RAW MATERIAL	WEIGHT IN POUNDS (LBS.)
SAND	1000
SODA ASH	290 TO 350
DOLOMITE	215 TO 260
LIMESTONE	70 TO 90
SALT CAKE	2 TO 15
ROUGE (97% Fe_2O_3)	3.5 TO 11.5
MANGANESE DIOXIDE	0.65 TO 6.5
COBALT OXIDE	0.004 TO 0.025
ANTHRACITE COAL	1 TO 2.5
NEPHELINE SYENITE	0 TO 150

[0016] A preferred anthracite coal is commercially available from the Shamokin Filler Company under the trade designation Carbocite and comprises about 70 to 72 weight percent carbon. Alternately, graphite or other carbonaceous material may be

suitably used as a source of reactive carbon. For graphite, a suitable addition is from 0.7 to 2.1 pounds of graphite per 1000 pounds of sand. Salt cake comprises sodium sulfate. In the presence of anthracite coal, the sulfate forms sulfur oxide that purges gasses from the melt that would otherwise form defects in the product. Additional coal in excess of the amount required for sulfate reaction is added to shift the iron oxide equilibrium to reduce the iron oxide derived form the rouge and form the desired ferrous oxide. Alternately, a coal slag commercially available from Calumite Corporation under the trade designation Melite, may be used instead of rouge in an amount up to about 55 pounds per 1000 pounds of sand. About 80% of the total iron oxide in Melite is ferrous oxide, thereby allowing the amount of the carbon addition to be reduced. Iron oxide may also be suitably added as cullet. Generally, increasing the quantity of sodium sulfate in the glass tends to shift the iron oxide equilibrium slightly toward oxidizing, whereas increasing carbon concentration in the glass batch shifts the iron oxide equilibrium toward reducing. Another influence on the iron oxide equilibrium is the peak furnace temperature. Increasing furnace temperature shifts the iron oxide equilibrium toward reduced ferrous oxide, whereas decreasing furnace temperature shifts toward the oxidized state.

[0017] Blue glass having enhanced blue coloration in accordance with this invention was made in laboratory melts in accordance with the following procedure. A base composition was formed of 100 grams sand, 32.22 grams soda ash, 8.81 grams limestone, 23.09 grams dolomite, 0.75 to 2.0 grams of sodium sulfate, 0.1 to 0.25 grams of carbocite, and 2.64 grams of nepheline syenite. To the base was added rouge, manganese dioxide, and cobalt oxide in amounts to achieve a desired colorant composition. The raw materials were dry mixed in a glass jar for 10 minutes

using a Turbula mixer, and loaded into a platinum-rhodium crucible. A small amount of water was added to the dry mixture. The mixture was then melted in a gas-fired furnace for 1 hour at 2600^{0}F. The melt was fritted, and the crucible plunged into cold water, whereupon the glass formed solid particles. The crucible was reheated to remelt the glass, and the fritting process was repeated. Thereafter, the glass was melted for 4 hours at 2600^{0}F. The melt was poured into a graphite mold and cooled slowly. The solidified glass was annealed by heating quickly to 1050^{0}F, holding for 2 hours, and then slowly cooling over a period of about 14 hours. Samples were ground and polished to about 4.0 mm thickness and tested to measure spectral properties. Results are reported in Table II, wherein % LTA is the percentage of transmittance using illuminant A and % LTC is the percentage transmittance using illuminant C, and % Fe_2O_3 is the weight percentage of total iron oxide.

Table II

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
% LTA	73.19	74.48	69.89	69.31	68.92	68.68
% LTC	75.68	76.92	72.77	72.17	71.83	71.53
Dominant Wavelength	487.8	488.2	488.6	488.1	488	487
% Excitation Purity	8.5	8	9.8	10	10.3	10.5
% UltraViolet Transmittance	62.86	63.04	56.52	55.75	56.39	56.51
% Infrared Transmittance	20.58	21.11	13.21	14.2	13.64	15.61
% Total Solar Energy	45.42	46.2	39.52	39.93	39.49	40.71
% Fe_2O_3	0.453	0.453	0.603	0.603	0.603	0.603
% FeO	0.236	0.24	0.318	0.305	0.312	0.288
Redox Ratio	0.521	0.530	0.527	0.506	0.517	0.478
% MnO_2	0.15	0.15	0.15	0.15	0.15	0.15
ppm Co	4	6	3	6	7	13

[0018] Examples 7 through 12 were prepared in accordance with the aforementioned procedure and contained equal amounts of total iron oxide, and with varying amounts of cobalt oxide additions and varying redox ratios. The samples exhibited similar blue coloration despite the variations in cobalt oxide and redox ratio. As shown by the results, visible transmittance decreased as cobalt oxide content increased.

Table III

	Example 7	Example 8	Example 9	Example 10	Example 11	Example 12
% LTA	73.79	72.74	73.63	72.13	72.03	71.19
% LTC	76.33	75.36	76.13	74.76	74.61	73.85
Dominant Wavelength	488.7	489	488.2	488.8	487.9	488.1
% Excitation Purity	8.2	8.4	8.3	8.6	8.9	9.1
% UltraViolet Transmittance	60.75	60.62	60.24	60.41	60.02	60.07
% Infrared Transmittance	18.15	17.02	19.78	16.7	18.48	17.06
% Total Solar Energy	44.14	42.94	45.02	42.55	43.68	42.46
% Fe_2O_3	0.503	0.503	0.503	0.503	0.503	0.503
% FeO	0.262	0.273	0.247	0.276	0.258	0.272
Redox Ratio	0.521	0.543	0.491	0.549	0.513	0.541
% MnO_2	0.15	0.15	0.15	0.15	0.15	0.15
ppm Co	2	2	4	4	6	6

[0019] Examples 13 through 18 were prepared by the aforementioned procedure, but with an increased total iron oxide content as compared to Examples 7 through 12. The results are reported in Table IV.

Table IV

	Example 13	Example 14	Example 15	Example 16	Example 17	Example 18
% LTA	73	71.87	71.56	72.22	71.37	71.79
% LTC	75.39	74.44	74.1	74.91	73.98	74.44
Dominant Wavelength	489.3	488.6	488.5	488.4	488.1	487.9
% Excitation Purity	7.6	8.5	8.5	9	8.9	9.1
% UltraViolet Transmittance	56.14	57.4	56.74	58.41	57.03	57.81
% Infrared Transmittance	19.36	17.26	17.9	16.72	18.17	18.03
% Total Solar Energy	44.22	42.68	42.96	42.62	43.1	43.27
% Fe_2O_3	0.553	0.553	0.553	0.553	0.553	0.553
% FeO	0.25	0.27	0.264	0.277	0.262	0.263
Redox Ratio	0.452	0.488	0.477	0.501	0.474	0.476
% MnO_2	0.15	0.15	0.15	0.15	0.15	0.15
ppm Co	2	2	4	4	6	7

[0020] Therefore, this invention provides a blue glass that includes a soda-lime-silica base and also includes a colorant portion consisting of iron oxide, manganese oxide and cobalt oxide, and exhibits high infrared absorption and enhanced blue coloration.

[0021] While this invention has been described in terms of certain embodiments thereof, it is not intended to be so limited, but rather only to the extent set forth in the claims that follow.